TMT4320 Nanomaterials, autumn 2024

Exercise 1: Finite size effects

Problem 1

Note – This problem is suitable for a computer-based solution. It is not recommended to answer it by hand using graphing paper and a pencil.

We will first perform some calculations related to nanoparticles (NPs) of sodium chloride (NaCl). Imagine that we can create *cubic* NaCl particles of arbitrary size by starting with a macroscopic rock salt crystal and splitting it along the {100} facets into progressively smaller cubes with side length a.[1]

(a) Assume that NaCl has a surface energy of $\gamma = 2 \times 10^{-5}$ J cm^{-2} for the {100} facets, and plot the total surface energy of 1 g of NaCl as a function of a.
- Density of NaCl: $\rho_{NaCl} = 2.17$ g cm^{-3}

(b) For non-spherical nanoparticles, such as NaCl cubes, it also makes sense to assign an energy to the edges. Assume that the edge energy for the edges between {100} facets in NaCl is $\sigma = 3 \times 10^{-13}$ J cm^{-1}. Add the total edge energy for 1 g of NaCl to the plot from (a), as well as the sum of the surface and edge energies.

(c) Add a horizontal line to the plot to indicate the enthalpy of fusion for NaCl. At which particle size does the sum of the surface and edge energy become comparable (say, within 10 %) of the energy required to melt the salt?

(d) Based on the result above, do you expect the melting point for NaCl NPs to be higher or lower than for bulk NaCl?

(e) What are the main approximations we have done in this calculation? Do you expect these results to hold true experimentally?

We now turn from NaCl to metallic palladium (Pd), which we will assume forms as *spherical* NPs with diameter a.

(f) Calculate and plot the fraction of surface atoms as a function of a (essentially what is plotted in Figure 2.1 in Cao & Wang). Some useful data on Pd:
- Atomic radius: $r_{Pd} = 1.37$ Å $= 1.37 \times 10^{-10}$ m
- Density: $\rho_{Pd} = 12.0$ g cm^{-3}
- Molar mass: $M_{m,Pd} = 106.4$ g mol^{-1}
- The Avogadro constant: $N_A = 6.022 \times 10^{23}$ mol^{-1}
- *Hint:* For simplicity, assume that each spherical NP is covered with a monolayer of Pd atoms in a square grid. That is, assume that each surface atom of diameter $2r_{Pd}$ covers an area of $2r_{Pd} \times 2r_{Pd}$ on the NP surface.

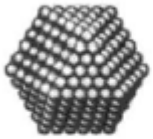
(g) What is the lower limit of a for which the result in (f) makes sense?

(h) As we approach very small cluster sizes, the continuous model in (f) becomes increasingly questionable. Add six discrete data points to the plot, based on exact results for six "full-shell" clusters, assuming a cubic close-packed structure (ccp), as shown in

[1] This is a top-down approach, although not a very realistic one! Think of it as a "thought experiment".

Table 1. (Some of these points are also included in CW Figure 2.1.) In which NP size range would you say that a "significant number of atoms" are on the surface?

Table 1: Selected full-shell clusters for NPs with cubic close packing of atoms.

Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

Problem 2

(a) In qualitative terms, how is the lattice parameter of a metal nanoparticle with a clean surface affected by the nanoparticle size?

(b) For a given solid with a *fixed surface area*, what are the main ways in which the surface energy can be reduced?